SO_2 Emissions Removal in a Hollow Fiber Membrane Contactor

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Abstract

SO_2 is the component of greatest concern and is used as an indicator for the larger group of gaseous sulfur oxides (SO_x) which should be reduced in the air. In this paper, DMA (Dimethylamine) solution was used as absorbent under the conditions of 0.1 L min^{-1} gas velocity, 0.1 L min^{-1} liquid velocity, and 290 K operating temperature. The effects of gas and liquid phase properties and module configuration on SO_2 absorption efficiency in the α-Al_2O_3 hollow fiber membrane contactor were investigated. Simulation results show that the changes of gas phase velocity, liquid phase velocity, concentration have great influences on the absorption efficiency of SO_2. Gas and liquid phase flow rate decreases and increases SO_2 absorption efficiency, respectively. Because gas in the membrane module stays for a longer time, more absorption time promotes the gas and liquid reaction. However, the changes of the liquid velocity and the volume fraction of SO_2 in the mixed gas are not significant to SO_2 absorption. In addition, the fluid in the turbulent state provides better SO_2 absorption efficiency than that in the laminar condition.

Keywords: SO_2 emission; air pollution; membrane; dimethylamine

1. Introduction

Currently, fossil fuels (coal, oil, and natural gas) are the primary energy sources throughout the world. As a result, fuel combustion will continue to emit sulfur dioxide (SO_2) and nitrogen oxides (NO_x) at an astonishing annual rate. In addition, SO_2 emissions lead to acid rain, air pollution, urban smog, and harm to human health and ecosystems (Bokotko *et al*., 2005; Rahmani *et al*., 2015). Thus, it is very urgent to removal SO_2 from air. Currently, there are several common methods for SO_2 removal, i.e., wet scrubbing (Jin *et al*., 2006), dry scrubbing (Neathery 1996), and wet sulfuric acid process (Kikkawa *et al*., 2002). But there are some shortcomings using these approaches, i.e., foaming, entrainment, flooding, and channeling issues, and a large required space. Membrane gas absorption (MGA) is an effective way for SO_2 removal providing a large gas and liquid contact surface using a hollow fiber membrane contactor with a high packing density. In addition, the membrane only acts as a fixed interface while gases transfer takes place across the membrane. Gas and liquid can be operated separately using the contactor.(Park *et al*., 2007) The MGA method was first used for gas absorption in 1985 by Qi and Cussler (1985). The gas and liquid system were operated without flooding problems even at high gas flow rates. This was due to the indirect contact between gas and liquid. CO_2 capture using MGA method has been a popular topic and widely investigated (Zhang *et al*., 2014, 2014a; Hoff *et al*., 2004). However, there were much fewer publications reported on the membrane absorption process of SO_2 (Luis *et al*., 2010; Yu *et al*., 2016). Karoor and Sirkar (1993) carried out SO_2 absorption experiments in pure water in a packed tower and a hollow fiber contactor. They found that efficient contacting was achieved in the case of a hollow fiber membrane contactor when compared to conventional reactors. In addition, the K_La value using MGA was around 10 times higher than that using conventional methods. Park *et al*. (2008) performed a series of SO_2 absorption experiments in a polyvinylidenefluoride (PVDF) hollow fiber membrane. A variety of chemicals including NaOH, Na_2CO_3, Na_2SO_3, and $NaHCO_3$ were compared regarding the SO_2 absorption performance. It was proved that the Na_2CO_3 solution showed the best performance for SO_2 absorption. Most previous studies have focused on experimental research and a few modeling works have been conducted (Fasihi *et al*., 2012; Luis *et al*., 2010; Yu *et al*., 2016). In our previous work (Zhang *et al*., 2015), the effects of membrane and contactor geometry parameters on SO_2 absorption performance were studied theoretically. The proposed model could provide guidelines for selecting the optimum contactor parameters.The purpose of this current work is to focus on the fluid properties and module configuration influences on SO_2 absorption efficiency in a hollow fiber membrane. The governing equations for material balances in three sections, i.e., the tube, membrane, and shell sides, were calculated and solved with the given boundary conditioning.

2. Physical Model

Figure 1 shows a physical model of SO_2 absorption inside a hollow fiber membrane contactor. A mixed gas containing SO_2 and air entered into the module and reacted with the absorbent of DMA. The mixed gas flowed out of the hollow fibers (shell side), and the absorbent flowed on

the other side of the membrane contactor (tube side). Meanwhile, SO_2 was absorbed into the absorbent in the tube side to complete the desulfurization after mixed gas entered into the fibers. When gas and liquid were operated under the ideal conditions, the model could be simplified to the process of a hollow fiber absorbing SO_2.

3. Numerical Model

In this case, some assumptions are made to simplify the mass continuity equations for calculating the developed model: The liquid phase in the tube is a steady flowing fluid under the constant temperature condition, with stable physical properties, and the liquid velocity distribution in the tube is characterised by a parabolic curve; The effect of the axial diffusion and radial convective mass transfer is neglected; The gas in the shell side is an ideal gas, and the fluid inside the tube is a Newtonian-type fluid. They have stable physical properties; both the velocity distribution and the concentration distribution in the tube are axisymmetric; The solute at the gas-liquid phase contact surface follows Henry's law.

The parameters of hollow fiber membrane contactor in this paper are presented in Table 1. The finite element method using COMSOL Multiphysics software was applied in the numerical solution of the control equations in the developed model. The numerical solver UMFPACK is mainly used in meshing error control. It is a promote format of implicit time and applies to solve the nonlinear, rigid and stiff boundary, which is also a good two-dimensional model numerical solver. The computer configuration of numerical simulation is a 64-bit operating system, with a 4.00GB memory space and Inter core AMD A8-4500M APU. Furthermore, Table 2 presents the physical and chemical property parameters of SO_2 as well as liquid absorbent, and reactive kinetic parameters between two phases. The software generates a series of isotropic triangular grid with a triangle smallest unit and creates cells according to a certain proportion. There are 24156 grids in this figure. Meanwhile, the area with dense meshes means large changes in the fluid concentration. This is due to that the absorbent inside the membrane contactor reacting with SO_2.

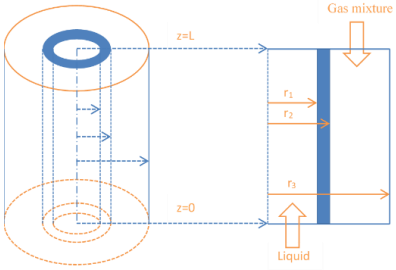


Figure 1. The internal structure of Hollow Fiber Membrane absorbing SO_2

Table 1. Parameters of hollow fiber membrane contactor (Luis *et al.*, 2008)

Parameter	Symbol	Value
Fiber materials		α-Al_2O_3
Canning material		316 stainless steel
Packing material		epoxide resin
Fiber outside diameter (μm)	d_o	4000
Fiber inside diameter (μm)	d_i	3000
Fiber length (m)	L	0.44
Fiber number	n	280
Effective membrane contact area (m^2)	S	0.8
Fiber pore size (nm)	d_p	100

Table 2. Parameters of hollow fiber membrane contactor

Name	Parameter	Number	Ref.
Henry's coefficient between SO_2 and water	$m_{SO_2-H_2O}$	25.86	Hikita *et al.*, 1977
Diffusion coefficient between SO_2 and water	$D_{SO_2-H_2O}$ ($m^2 s^{-1}$)	2×10^{-9}	Dutta *et al.*, 1987
Henry's coefficient between SO_2 and DMA solution	m_{SO_2-DMA}	0.00131	Koonaphapdeelert *et al.*, 2009
Diffusion coefficient between SO_2 and DMA solution	D_{SO_2-DMA} ($m^2 s^{-1}$)	2.1×10^{-9}	Bird *et al.*, 2002
SO_2 diffusion coefficient in the gas mixture	D_{SO_2-Gas} ($m^2 s^{-1}$)	1.26×10^{-5}	Luis *et al.*, 2010

4. Results and discussions

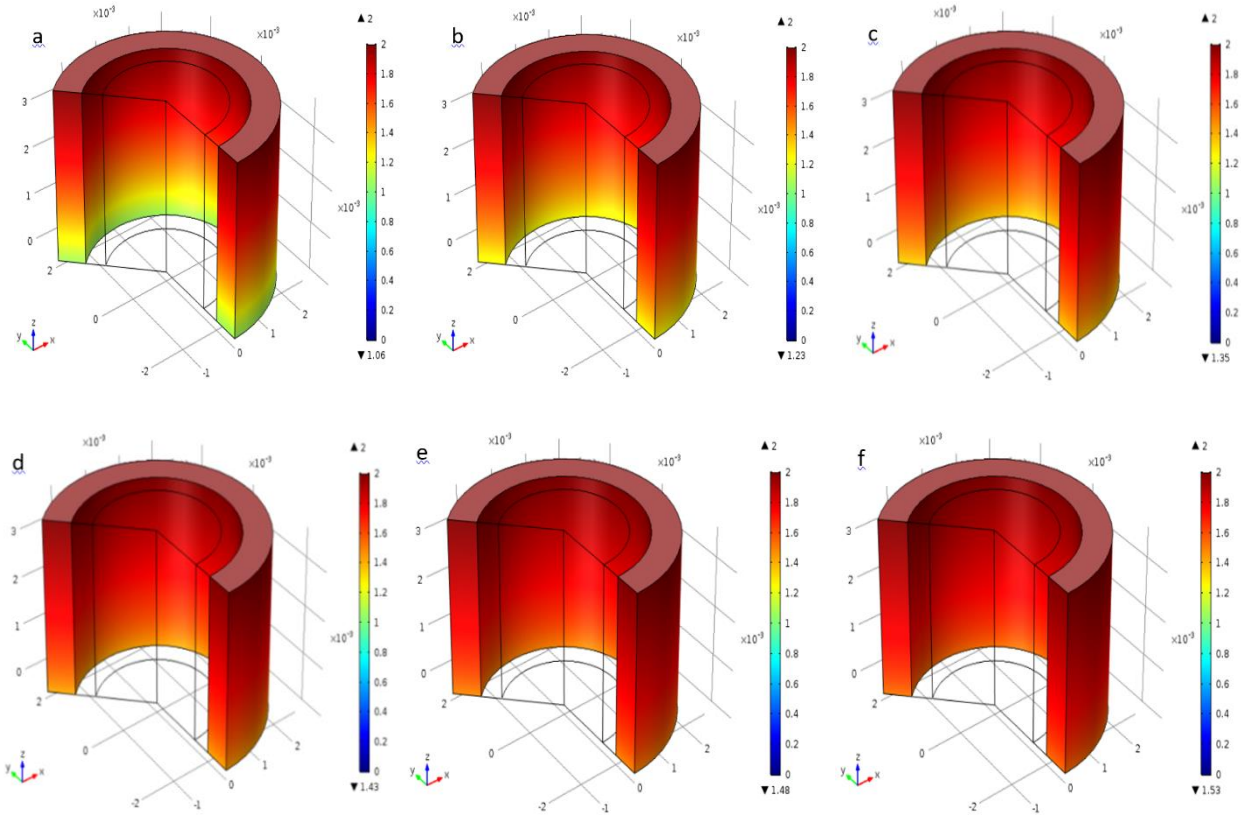
4.1. Concentration distributions

It is an effective way to describe visually the SO_2 concentration distribution inside the membrane contactor with three-dimensional concentration schematic. Figure 2 (a-f) shows the SO_2 three-dimensional concentration schematic inside the membrane contactor when reacting with 2 mol L^{-1} DMA solution at various gas velocities, respectively. As observed, the SO_2 concentration in the shell side of the membrane contactor gradually decreases from 2.0 to 1.06, 1.23, 1.35, 1.43, 1.48, and 1.53 mol L^{-1}. It is obvious that SO_2 in the mixed gas reacts continually with the DMA solutions, resulting in the continuous decrease in SO_2 contributes at the exit of the shell side. According to Figure 3, the SO_2 concentration increases from z=0 to z=L. This was due to the DMA solution absorbed SO_2 in the tube, and then the SO_2 concentration at the exit of tube reached to the highest value. Due to the concentration gradient of SO_2 between the tube and membrane sides, SO_2 concentration gradually reduced from the interface between the tube and membrane sides to the central axis of the membrane contactor.

4.2. Effect of the gas flow velocity (model verification)

Figure 4 demonstrates the comparison between the simulation results of SO_2 removal efficiency and the experimental data at different gas velocities. It can be seen from this figure that when the gas velocity increased from 0.0006 to 0.0035 m s^{-1}, SO_2 removal efficiency decreased from 46.82 to 23.5%. The reason was that when the velocity of gas phase increased, the gas and liquid reaction time reduced significantly, which led to inadequate reacting in the absorption process and affected the SO_2 removal efficiency. Although the SO_2 removal efficiency was high with a low gas velocity, the mass transfer effect of the whole process was relatively poor. The conclusion in literature (Eslami *et al*., 2011) had a similar result trend. Thus, it was necessary to consider comprehensively the influence of the gas velocity on the removal efficiency and the mass transfer rate of SO_2 while selecting the optimal gas velocity condition of the whole system.

Figure 2. The three-dimensional concentration distribution of SO_2 reacting with DMA in the shell side (mixed gas of 5% SO_2 and air, the liquid phase flow rate is 1 L min^{-1}, the operating temperature is 290 K. V_g represents the gas phase flow velocity, a: V_g=0.0006 m s^{-1}; b: V_g=0.0012 m s^{-1}; c: V_g=0.0018 m s^{-1} ; d: V_g=0.0023 m s^{-1}; e: V_g=0.0029 m s^{-1}; and f: V_g=0.0035 m s^{-1}).



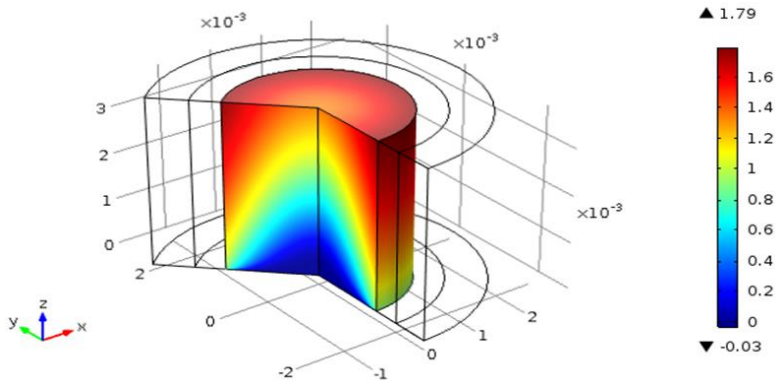


Figure 3. The three-dimensional concentration distribution diagram of the SO_2 concentration in tube side (mixed gas of 5% SO_2 and air, the gas phase flow rate is 0.1 L min^{-1}, the liquid phase flow rate is 1 L min^{-1}, the operating temperature is 290 K).

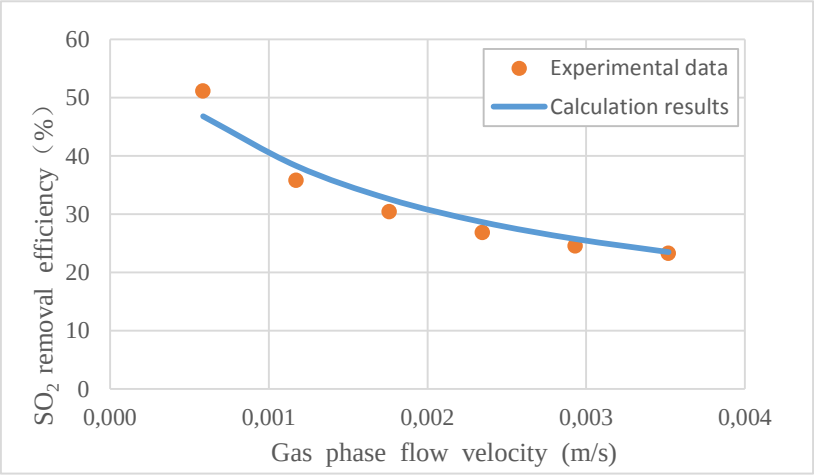


Figure 4. Effect of the gas phase velocity on SO_2 absorption efficiency (mixed gas of 5% SO_2 and air, the liquid phase flow rate is 1 L min^{-1}, the operating temperature is 290K).

5. Conclusions

In allusion to atmospheric pollution aggravating, this paper mainly focused on the absorption problems of SO_2. A promising method of membrane technology has been used in this paper. The effect of the gas and liquid phases properties and module configuration on SO_2 absorption was investigated numerically. In this study, the three-dimensional distribution of SO_2 concentration in the hollow fiber membrane contactor was observed visually by applying COMSOL Multiphysics. The distribution of SO_2 concentration was shown intuitively with changing the gas and liquid phase parameters. Then, the model validation was carried out between the experimental data and the simulation results at different gas flow velocities and showed that the developed model was feasible and reliable. In all, this model could efficiently predict the influence of the gas and liquid parameters and module configuration on SO_2 absorption, which could optimize the system data and provide guidelines for the operation of the actual application in the future.

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References

Bird, R. B.; Stewai, W. E.; Lightfoot, E. N. Transport Phenomena; John Wiley & Sons, Inc.: New York, **2002**.

Bokotko, R. P.; Hupka,J.; Miller, J. D. Flue gas treatment for SO_2 removal with air-sparged hydrocyclone technology. *Environ. Sci. Technol.* **2005,** 39, 1184.

Dutta B. K.; Basu R. K.; Pandit A.; Ray, P. Absorption of sulfur dioxide in citric acid-sodium citrate buffer solutions. *Ind. Eng. Chem. Res.* **1987**, 26, 1291.

Eslami S.; Mousavi S. M.; Danesh S.; Banazadeh, H. Modeling and simulation of CO_2, removal from power plant flue gas by PG solution in a hollow fiber membrane contactor. *Adv. Eng. Softw.* **2011**, 42, 612.

Fasihi, M.; Shirazian, S.; Marjani, A.; Rezakazemi, M. Computational fluid dynamics simulation of transport phenomena in ceramic membranes for SO_2 separation. *Math. Comput. Model.* **2012,** 56, 278.

Hikita H.; Asai S.; Tsuji T. Absorption of sulfur dioxide into aqueous sodium hydroxide and sodium sulfite solutions. *AIChE J.* **1977**, 23, 538.

Hoff, K. A.; Juliussen, O.; Falk-Pedersen, O.; Svendsen, H. F. Modeling and experimental study of carbon dioxide absorption in aqueous alkanolamine solutions using a membrane contactor. *Ind. Eng. Chem. Res.* **2004,** 43, 4908.

Jin, D. S.; Deshwal, B. R.; Park, Y. S.; Lee, H. K. Simultaneous removal of SO_2 and NO by wet scrubbing using aqueous chlorine dioxide solution. *J. Hazard. Mater.* **2006**, 135, 412.

Karoor, S.; Sirkar, K. K. Gas absorption studies in microporous hollow fiber membrane modules. *Ind. Eng.* Chem. *Res.* **1993,** 32, 674.

Kikkawa, H.; Nakamoto, T.; Morishita, M.; Yamada, K. New wet FGD process using granular limestone. *Ind. Eng. Chem. Res.* **2002,** 41, 3028.

Koonaphapdeelert S.; Wu Z.; Li K. Carbon dioxide stripping in ceramic hollow fibre membrane contactors. *Chem. Eng. Sci.* **2009**, 64, 1.

Luis P., Garea A., Irabien A. Sulfur dioxide non-dispersive absorption in N, N-dimethylaniline using a ceramic membrane contactor. *J. Chem. Tech. Biot.* **2008**, 83, 1570.

Luis, P.; Garea, A.; Irabien, A. Modelling of a hollow fibre ceramic contactor for SO_2 absorption. *Sep. Purif. Technol.* **2010,** 72, 174.

Neathery, J. K. Model for flue-gas desulfurization in a circulating dry scrubber. *AIChE J.* **1996,** 42, 259.

Park, H.; Deshwal, B.; Kim, I.; Lee, H. Absorption of SO_2 from flue gas using PVDF hollow fiber membranes in a gas–liquid contactor. *J. Membr. Sci.* **2008,** 319, 29.

Park, H.-H.; Lim, C.-W.; Jo, H.-D.; Choi, W.-K.; Lee, H.-K. Absorption of SO_2 using PVDF hollow fiber membranes with PEG as an additive. *Korean J. Chem. Eng.* **2007,** 24, 693.

Qi, Z.; Cussler, E. L. Microporous hollow fibers for gas absorption: I. Mass transfer in the liquid. *J. Membr. Sci.* **1985,** 23, 321.

Rahmani, F.; Mowla, D.; Karimi, G.; Golkhar, A.; Rahmatmand, B. SO_2 removal from simulated flue gas using various aqueous solutions: Absorption equilibria and operational data in a packed column, *Sep. Purif. Technol.* **2015**, 153,162.

Yu, H.; Thé, J.; Tan, Z.; Feng, X. Modeling SO_2 absorption into water accompanied with reversible reaction in a hollow fiber membrane contactor. *Chem. Eng. Sci.* 2016, 156, 136.

Zhang, Z.; Yan, Y.; Zhang, L.; Chen, Y.; Ran, J.; Pu, G.; Qin, C. Theoretical study on CO_2 absorption from biogas by membrane contactors: Effect of operating parameters. *Ind. Eng. Chem. Res.* **2014,** 53, 14075.

Zhang, Z.; Yan, Y.; Wood, D. A.; Zhang, W.; Li, L.; Zhang, L.; Van der Bruggen, B. Influence of the Membrane Module Geometry on SO_2 Removal: A Numerical Study. *Ind. Eng. Chem. Res.* **2015,** 54, 11619.

Zhang, Z. E.; Yan, Y. F.; Zhang, L.; Ju, S. X. Hollow fiber membrane contactor absorption of CO_2 from the flue gas: Review and perspective. *Global NEST J.* **2014a,** 16, 355.